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Self-Assembly of Metal Nanoclusters in Block Co-Polymers

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ABSTRACT

This paper describes the formation of cobalt and iron metal nanoclusters in various polymeric domains. The size of the particles, their size distribution and their geometry is controlled by the extent of the interfacial interactions between the polymeric phase and the growing metal fragments. Iron oxide particles are shown to exhibit various geometries as a function of the polymer medium and the temperature at which they are formed. The selective phase separation and particle confinement of cobalt clusters in the presence of PS₂₅₃₀₀-b-PMMA₂₅₉₀₀ block co-polymer was achieved due to the different reactivities of the functional groups in the blocks towards the metal fragments. Transmission electron micrographs showed that cobalt clusters aggregated primarily in the poly(methyl methacrylate) block, while no cobalt nanoclusters were observed in the polystyrene block, thus creating a patterned distribution that coincided with the morphology of the block copolymer.

INTRODUCTION

Hierarchical materials are ordered on the molecular (10-100Å), nano (10nm-100nm) and meso (1μm-10μm) scales. This unique level of organization leads to specialized material properties that significantly differ from those of less ordered phases. However, optimal performance requires a degree of control over domain size and distribution, on all length-scales, which is not easily obtainable with current synthetic methods.

The development of a synthesis methodology to control the structure and properties of metallic nanocluster-polymeric composites requires detailed understanding of the interactions between the metal clusters and their polymeric environment, as well as the relationship between polymeric parameters and cluster formation. Although various studies have shown that polymers control cluster formation and properties [1-4], little is known regarding the details of this relationship. The large number of parameters (e.g. polymer molecular weight, chemistry and concentration) requires a systematic investigation. This paper describes the development of a *versatile and controllable* synthetic process for the formation of *three-dimensional, self-assembled nanoparticle arrays* in, and aided by, a *polymeric medium*. The development of appropriate synthetic and processing methods, which can produce finite, ordered domains with a given geometry, is a central theme in the design of hierarchical ordered structures [5-8].

EXPERIMENTAL METHOD

The solution decomposition of Co₂(CO)₈ and Fe(CO)₅ to metal nanoclusters was performed in a sealed three-neck round-bottomed reaction vessel that was first evacuated and then flushed with N₂. A side neck was equipped with a thermometer, the middle neck with a reflux condenser, and the other neck with a gas inlet-outlet glass fitting. The thermometer outlet was also used for sampling. In order to drive the reactions away from

equilibrium and toward completion, the carbon monoxide gas formed during the reaction had to be continuously flushed away by the N₂ stream, while avoiding bubble formation. The jacketed reaction flask was equipped with tubing to circulate heated ethylene glycol around the reaction flask, thus keeping the contents of the flask at a constant temperature. The flask was connected to a vacuum line via the reflux condenser, which allowed strict control of the environment inside the flask at all times. The initial concentration of the metal carbonyl in the solution was 5×10^{-3} M. The solution was allowed to react under a continuous nitrogen stream with constant stirring.

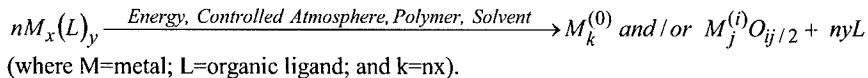
The decomposition of the metal carbonyl precursors in both polystyrene and poly(methyl methacrylate) homopolymers, and in the PS₂₅₃₀₀-b-PMMA₂₅₉₀₀ block co-polymer was monitored via Fourier transform infrared spectroscopy (FTIR) at low temperatures. The decomposition in poly(styrene), $\bar{M}_n = 250,000$, was carried out in toluene at 90 °C and the decomposition in poly(methyl methacrylate), $\bar{M}_n = 300,000$, was carried out in methylene chloride at 40 °C. The decomposition in the PS₂₅₃₀₀-b-PMMA₂₅₉₀₀ block co-polymer solution was carried out in toluene at 90 °C as well. The reaction at the low temperature spanned more than two weeks, but data was collected for only the first 192 hours. Aliquots from the reaction solution were placed into a demountable infrared liquid cell with NaCl windows and a 0.2 mm optical path. The flask was placed under nitrogen during sample removal to prevent oxidation of the metal clusters. The cell was not demounted during the experiment, and the sample removal and cell washing was performed by suction. FTIR spectra were collected on a Nicolet Nexus 870 spectrophotometer, with a resolution of 2 cm⁻¹ and 50 scans/spectrum.

After the decomposition reactions of Co₂(CO)₈ in 0.38 wt. % PS-b-PMMA co-polymer was complete, TEM samples were made by placing an aliquot of the solution onto a carbon coated TEM grid. These films constituted “bulk” block copolymer films. A high quality, free-standing film was also prepared to be microtomed by combining 1 mL of the block copolymer solution with 2 mL of a 30 wt. % solution of PS in toluene, $\bar{M}_n = 300,000$. The final composition of these films was then 33% PS₂₅₃₀₀-b-PMMA₂₅₉₀₀ containing cobalt nanoparticles, and 67% PS homopolymer. The solution was added dropwise onto a glass slide until a film covered the entire surface. After allowing the solvent to evaporate, the film was removed from the slide by peeling off one corner of the film and applying water between the film and the slide. The hydrophobic interactions between the film and water caused the film to peel off easily. These films were microtomed and constituted “thinly sectioned” block copolymer films. The TEM imaging was conducted on both Hitachi HF-2000 field emission gun (FEG) and JEOL 2010, and a high resolution JEOL 4000EX. The operating voltage was 200 keV for all three microscopes.

RESULTS AND DISCUSSION

The chemical reactivity of metal clusters is largely determined by the size of the particles, and therefore the ability to control particle size, particle size distribution and dispersion would imply an ability to determine the reactivity and interfacial behavior of the clusters in the polymer-metal cluster interfacial systems. The synthesis of metal clusters, which is designed to accommodate these size manipulations, consists of the decomposition of organometallic complexes under controlled conditions (the energy

source could be thermal, UV radiation or E-beam), to form uniform metal dispersions of very small particle size [9,10]. The process is best described in the following three stages (Figure 1): (a) The preparation of homogeneous solutions of metal complexes in a carefully selected solvent; (b) The mixing of the organometallic complex solution with a polymer solution in which the polymer of choice has been dissolved in the common solvent; and (c) The energy-induced decomposition of the organometallic complexes to form uniform metal dispersions of very small particle size in the polymer solution. The overall reaction may be described as follows:



This approach may afford unique opportunities for investigating fundamental aspects of nucleation and growth of metal clusters, as well as the properties of such nanoparticles as functions of cluster size, concentration and environment. Metallic fragments created by the energy-induced decomposition of metal complexes are highly reactive [11,12], which constitutes the driving force for the nucleation and growth mechanism to form nanocrystals. The size of the clusters formed is significantly influenced by the following parameters: (a) Reducing or oxidative atmospheres, (b) The diffusion of small cluster fragments through the medium and (c) The viscosity of the medium in which the diffusion takes place. Chemical reactivity, for instance, is found to be strongly related to the size of these metal clusters, since the size of the clusters largely determines their crystal structure.

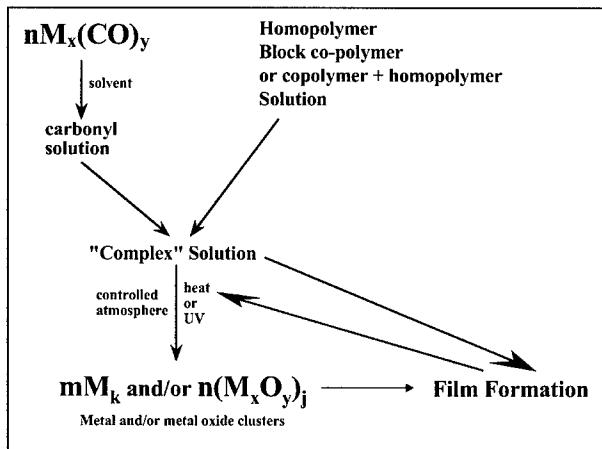


Figure 1: Schematic description of the synthesis methodology for the self-assembly of metal nanoparticles.

The thermal decomposition of cobalt carbonyls to metallic Co in polystyrene (PS) solutions has been used as a *model system* to test the chemical method under investigation. This process consists of a stepwise colloidal reaction mechanism [13-15], which is highly facilitated by the presence of macromolecules that provide the necessary solid state support and microenvironment which constitutes the driving force for cluster aggregation. As particle size grows, the mobility of the reactive metal fragments and their ability to diffuse through the solution and collide with each other decreases, and equilibrium is reached when the diffusion of the particles is too slow for observation in real time.

Experimental results of this model system (Figure 2), show that there is an inverse correlation between cobalt cluster size (measured by *Transmission Electron Microscopy*, TEM) and the PS concentration in the reaction solutions [16], accompanied by a considerable particle size distribution narrowing. When the excess polymer is washed off and the solvent is removed, the particles do not undergo additional growth, which indicates that they have been sufficiently coated by the “capping” polymer to prevent further aggregation.

When all the solvent has been removed from the polymer-containing solutions prior to decomposition (to form a polymer film), the smallest cobalt nanoparticles are formed. The ultimate result is a phase separated material in which the metal cluster and polymer phases are held together via the irreversible interfacial bonds created during the decomposition process. Moreover, the metallic nanoparticles are homogeneously dispersed throughout the polymer film, and given their small size, they exhibit high surface reactivity, and ensure good mechanical coupling of the particles to the polymer matrix.

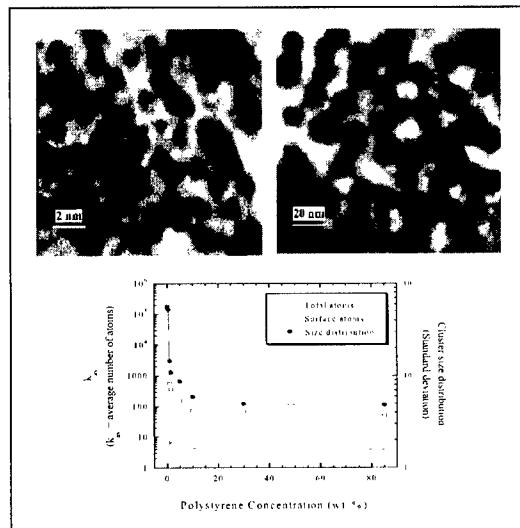


Figure 2: Co particles formed in polystyrene film (top left) and in a hydrocarbon solution (top right). The dependence of Co particle size, size distribution and abundance of surface atoms as a function of initial polymer concentration.

The synthetic method that we have developed for the controlled synthesis of metal nanoclusters can be extended to include also the manipulation of not only cluster size, size distribution and composition, but also geometrical shape. Biological systems have a unique ability to control crystal structure, phase, orientation and nanostructural regularity of inorganic materials [see, for example 17,18]. In biological hybrid systems it has been shown [17,18] that selected peptides can specifically bind to zinc-blende III-V semiconductor surfaces by discriminating between various crystallographic faces. These peptides are being used to grow nanoparticles and nanowires of specific crystallographic structure and orientation. Using these molecular interactions and specific nanoparticles, organic/inorganic hybrid materials may be organized into supramolecular architectures [for example, 19-21].

The preferred adsorption of the polymer chains to a particular crystallographic surface of the growing metal nano-clusters is clearly demonstrated in several Fe-polymer systems, as shown in Figure 3. The preferential adsorption of synthetic polymers to distinct crystallographic faces of the growing metallic fragment causes a distortion of the cluster shape, since the growth directions become differently hindered by the polymer. Hence, the result is a high degree of anisotropy in the cluster shape. In these systems, the protocol by which the decomposition reaction of $\text{Fe}(\text{CO})_5$ in the presence of polymers is carried out is essential in determining the metal nanoparticle shape. Systems in which the same polymer has been used but the conditions of the thermal decomposition reaction were different, exhibited different particulate shape. For example, in the presence of poly(vinylidene difluoride) (PVF2), the thermal treatment of the metal carbonyl-polymer complex solution that is concurrent with solvent removal and polymer film formation ("hot" method), gives rise to nanopyramids. On the other hand, the thermal treatment of the metal carbonyl-polymer complex solution that is performed after solvent evaporation at room temperature ("cold" method), gives rise to nanospheres [9]. In the former case, the solvent is present in the initial stages of the decomposition process, allowing a higher degree of mobility of the growing nanoclusters and the polymer chains, while in the latter case the metal carbonyl precursors are immobilized in the polymer film. Additional

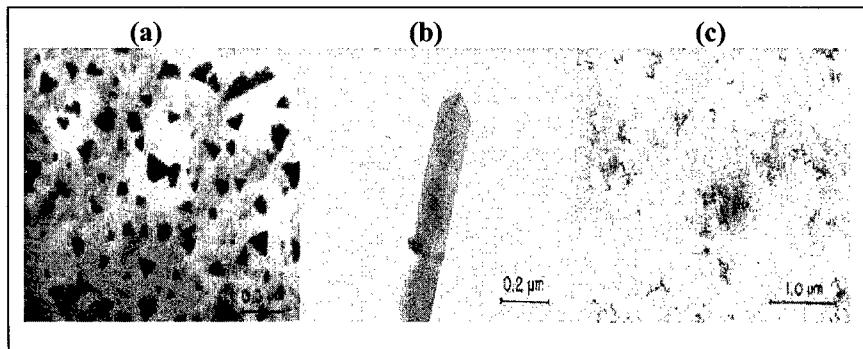


Figure 3: Shape control in the synthesis of iron nanoparticles via the decomposition of $\text{Fe}(\text{CO})_5$ in the presence of (a) PVF2-nanopyramids; (b) PMMA-nanorods; and (c) Poly(carbonate)-nanostings [9].

examples include the formation of Fe nanorods via the decomposition of $\text{Fe}(\text{CO})_5$ in the presence of poly(methyl methacrylate) (PMMA), and the formation of nanostrings in the presence of poly(carbonate) (PC). This latter nanostructure is accompanied by extensive scission of the polymer chains, which may be partly responsible for the formation of the small Fe particles organized as nanostrings [9]. These examples are comprised of preliminary results, and a comprehensive study of these phenomena are currently underway. It is our intention to concentrate on the Fe and Co systems in the presence of PVF₂, PMMA and PC, in order to establish the protocols for specific nanocluster polymer-induced geometry control as a function of polymer concentration and polymer molecular weight.

A direct extension of the methodology developed here is the creation of *polymer-induced, self-assembled, multi-functional nanoparticulate materials*, i.e. materials in which the metal clusters are phase separated within the polymer according to a predetermined spatial architecture. This spatial architecture can be achieved by the utilization of the phase separation and microdomain formation in multi-component polymers with self-organizing properties, i.e. *block copolymers*, for the anisotropic synthesis of nanoparticulate composites [22-24]. Hence, these block copolymers will be used as a structural and chemical template to produce a controllable, predetermined, self-developing spatial arrangement of clusters [24]. This implies that if the metal clusters are to aggregate in a particular polymeric domain, there should exist a driving force that would direct the phase separation such that certain areas in the polymer will be more reactive than others toward the metal clusters. This can be achieved by using *di-block copolymers* as a model system, in which one block will have reactive groups and the other block will be "inert" toward the metal clusters. One of the main features of block copolymers is the incompatibility between different parts of the same polymeric chain and the formation of microdomains [25]. The microdomain structure may consist of spheres, cylinders or lamellae, depending on the molecular weight of the blocks, their relative concentrations, the solvents used and the interfacial properties of the blocks. By carrying out the decomposition of the metal carbonyls in a di-block copolymer which was designed to phase separate in one of the main microdomain structures, we expect to obtain a high concentration of metal clusters in the domains occupied by the reactive block, and hence the spatial distribution of the clusters will conform to the spatial pattern created by the block copolymers. In this manner, it will be possible to concentrate the metal clusters in an ordered array of complex and highly ordered structures, as shown in Figure 4a. The homogeneous dispersion of the metal nanoclusters within the reactive block will provide certain physical and chemical properties inherent to metallic systems (e.g. mechanical strength, electrical conductivity, etc.), and thus create distinct functional regions within the polymeric material.

The selective incorporation of metal clusters into block copolymers may be achieved by three main pathways: (a) The exposure of block copolymer films to metal vapors, resulting in the selective adsorption of the metal atoms onto the more reactive block; (b) The impregnation of block copolymer films with a metal salt, with a subsequent reduction of the salt to form metallic clusters in the reactive block domains; and (c) The homogeneous mixing of the block copolymers with the organometallic precursors followed by the in-situ phase separation and self-assembly of both metal clusters and copolymer microdomains [22-24,26,27]. In the first two approaches, the

block copolymers are first allowed to self assemble into their distinct microdomains, and are subsequently exposed to the metallic moiety. Under these conditions, there are significant differences in the size and dispersion of the metallic clusters between the bulk copolymer films and the thin (microtomed) films, due to the rates of diffusion and penetration depth of the metallic precursors. Moreover, if the polymers are below their T_g , the interfacial adhesion between polymer chains and the growing clusters is severely hindered, and therefore, the limitation on metal cluster size is due to nucleation and growth kinetics and not to a polymer “capping” effect. The third method, and the one that we have developed, is designed to circumvent these issues by performing the nucleation and growth of the metal clusters and the phase separation of the block copolymers *in-situ*, in a homogeneous solution of both components. Under these conditions, nucleation and growth of the clusters will be limited not only by reaction kinetics, but also by the direct interaction with the available reactive sites on the polymer. Hence, the difference in the reactivity of the two blocks toward the metal will be fully exhibited.

Preliminary results for the cobalt-poly(styrene-*b*-methyl methacrylate) block copolymer system (Figure 4c), show a distinct segregation of the cobalt clusters in defined regions, similar to the “worm-like” distribution achieved by Cohen et al. in their microtomed Ag-block copolymer samples [24]. The actual microstructure exhibited by the metal-containing block copolymers is strongly influenced and complicated by the phase behavior of block copolymer in solution prior to metal incorporation, irrespective to the method used. In dilute solutions, the blocks form micelles [27] where one of the blocks forms the core of the micelle (the block less favored by the solvent used), and the other forms the shell. After the incorporation of the metal nanoparticles, the solvent is evaporated, and it is expected that a phase transition will take place resulting in a microstructure that corresponds to the block copolymer composition. However, our own preliminary results and the results in the literature [22-24,26,27] suggest that this phase transformation is incomplete, either due to some degree of crosslinking caused by the metal nanoparticles or by the change in phase behavior of the block copolymers as a result of the presence of the nanoclusters (Figure 4b,c).

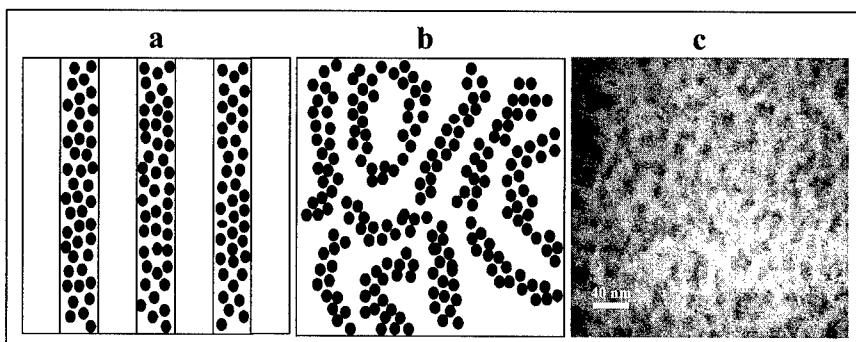


Figure 4: Cobalt nanoparticle size distribution in the PS-PMMA block co-polymer domains. (a) Idealized lamellar phases; (b) Arrested phase transformation; (c) TEM micrograph of particle distribution.

The average particle size is ~ 50 Å, and it does not change upon film formation. Moreover, particle size and microdomain distribution is independent of film thickness, and is a function of the initial polymer solution concentration in the decomposition reaction.

Additional insight into the strength of the interaction between the cobalt nanoparticles and the PMMA block was obtained by probing the diffusion of the cobalt particles from the PMMA domain into a large PS domain. For this purpose, the PS₂₅₃₀₀-*b*-PMMA₂₅₉₀₀ block copolymer solutions used in this work were doped with high molecular weight polystyrene homopolymer. The addition of a homopolymer to a diblock copolymer has the effect of increasing the domain size of the common block for a particular morphology [27-30], if the total concentration of the homopolymer component is within the concentration regime commensurate with that morphology. In this particular case, since the molecular weight of the polystyrene homopolymer far exceeded (six fold) the combined molecular weights of both blocks, the block copolymer and the homopolymer behaved as a macrophase and microphase separated blend [31-33]. Figure 5 shows a HRTEM image of a “thinly sectioned” microtomed film of a high molecular weight polystyrene ($\overline{M}_n = 300,000$) blended with the PS₂₅₃₀₀-*b*-PMMA₂₅₉₀₀ block copolymer, that contained cobalt precursors which were then decomposed *in situ* according to the cluster synthesis used in these experiments. The decomposition of the cobalt precursors in the polymer medium occurred either before or after the addition of the PS homopolymer. The distribution of the cobalt particles within the polymeric matrix was similar in both cases. The particles were concentrated in the block copolymer, specifically in the PMMA microdomain, without any traces of cobalt clusters in the polystyrene homopolymer phase. No cobalt particle diffusion from the poly(methyl methacrylate) domain to the polystyrene domain was observed, as evidenced by the irreversible confinement of the cobalt particles in the more reactive block.

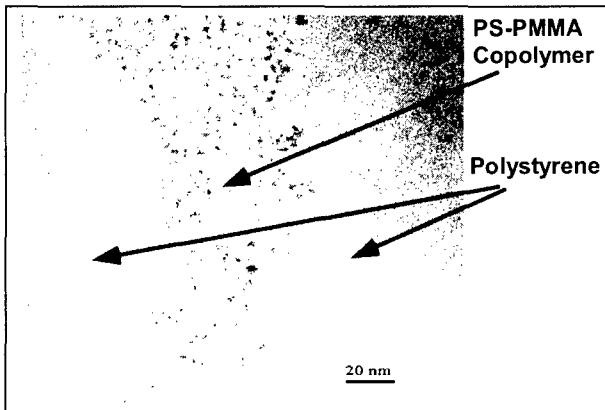


Figure 5: HRTEM image of a microtomed film of the homopolymer/block co-polymer blend showing cobalt particle confinement in the block phase.

SUMMARY

The results presented in this paper demonstrate that the incorporation of metal nanoclusters, synthesized via an *in situ* decomposition of metal carbonyl precursors into a block copolymer, generates an uneven dispersion of the particles, with a preferential aggregation in the poly(methyl methacrylate) block. This can be explained by the reactive adsorption of the PMMA block onto the metal cluster surface, through the interaction of the carbonyl group of the polymer with the metal. This is supported by experimental results obtained with Fourier Transform Infrared (FTIR) spectroscopy that are described elsewhere [34]. The morphology of the system did not conform to the expected lamellar structure, due to the fact that the PS₂₅₃₀₀-b-PMMA₂₅₉₀₀ block copolymer that was used forms micelles in the solvent of choice (in this case toluene), with the poly(styrene) block constituting the shell and the poly(methyl methacrylate) block constituting the core of the micelles. The preferential incorporation of the cobalt nanoclusters into the poly(methyl methacrylate) block has the effect of immobilizing the micellar structure, thus preventing the expected phase transformation to the expected lamellar morphology upon removal of the solvent. Moreover, when this block copolymer was mixed with a high molecular weight poly(styrene) homopolymer, the common poly(styrene) moieties did not enhance the mutual solubility of the homopolymer and the block copolymer, and the material behaved as a macrophase and microphase separated blend.

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